Band gap of Ge rich $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys

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$\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ films ($x \approx 0.90, \ y \leq 0.02$) were grown by molecular beam epitaxy on Si substrates. Infrared optical absorption was used to obtain the band gap energy at room temperature. Biaxial strain obtained from x-ray diffraction measurements verified the presence of nearly relaxed films, and the total and substitutional C contents were obtained from channeling C-resonance backscattering spectroscopy. We show by direct measurements that interstitial C had a negligible impact on the band gap, but substitutional C was found to increase the band gap with respect to equivalently strained $\text{Si}_{1-x}\text{Ge}_x$ alloys. While strain decreases the band gap, the effect of substitutional C on the band gap depends on the Si and Ge fractions. © 1996 American Institute of Physics. [S0003-6951(96)04343-4]

The energy band gaps of group IV alloys have been studied by photoluminescence (PL), absorption, spectroscopic ellipsometry,6,7 and theoretical techniques.8–10 Several studies suggest an energy band gap decrease as the C content is increased,6,9 others suggest an increase in the energy band gap.4,8 Attempts to clarify this behavior have depended on measurements of strained pseudomorphic thin layers with extrapolations to zero strain based on assumption of deformation potentials, which are not well known.

In this letter, we studied relaxed layers with Ge rich compositions. Techniques to probe the indirect optical band gap by absorption are challenged by weaker absorption than a direct band gap material, substrate absorption, and interference fringes within the thin film. We describe an approach to deducing the band gap from optical absorption observations which to some extent transcend these difficulties.

We have produced a series of crystalline $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys by solid source molecular beam epitaxy (MBE) on (100) Si substrates.4,11 The substrate temperature was 600 °C. Ge was thermally evaporated in a pyrolytic graphite crucible at 1260 °C, and Si was thermally evaporated in a pyrolytic graphite (PG) crucible at 1685 °C. The C source consisted of a PG filament heated by a direct current up to 49 A. Growth rates were typically 0.06 µm/h. Thicknesses were measured by a mechanical stylus method and were typically 0.18 µm.

Film compositions (Table I) were measured by Rutherford backscattering spectrometry (RBS). C elastic-resonance backscattering was used to measure the C concentration using a 4.3 MeV He beam. The total measured C concentrations were up to 2 at. %, with an accuracy of ±0.2 at. % C. The extent of substitutional C was studied using ion channeling characterizations. In samples SGC-67, SGC-68, and SGC-70, less than 25% of the C was substitutional, but at least 70% of the total C in SGC-69 was found to be substitutional. Further RBS details will be published elsewhere.12

X-ray diffraction (XRD) measurements were performed to determine the strain in the films. The lattice constants of the films in the growth direction ($a_i$) were computed from the peak position of the alloy (004) x-ray reflections. The lattice constants in the direction parallel to the substrate surface ($a_o$) were deduced from the (224) and (115) reflections. Assuming Poisson’s ratio to be 0.27, we calculated the relaxed cubic lattice constant ($a_o$) and the biaxial strain for each sample. We observed $a_i - a_o < 0.03$ Å for all samples, indicating nearly relaxed films. Relaxed films were expected as the films were well over the 20 Å critical thickness13 of Ge rich Si alloys.

The optical absorption at photon energies near the band gap was measured at room temperature by Fourier transform infrared (FTIR) spectroscopy. The alloys studied were Ge rich, thus their band gap energies were less than that of Si, and the substrates were transparent in the vicinity of the alloy’s fundamental absorption edge. The transmission data of the samples were ratioed to transmission curves of a reference substrate to remove sub-gap substrate absorption errors.

### Table I. The effect of substitutional and interstitial C on the energy band gap of Ge rich $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Strain</th>
<th>Band gap (meV)</th>
<th>Equivalently strained $\text{Si}_{1-x}\text{Ge}_x$ band gap (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGC-67</td>
<td>Si$<em>{0.135}$Ge$</em>{0.845}$C$_{0.02}$</td>
<td>1.5 x 10$^{-3}$</td>
<td>889 ± 3</td>
<td>896</td>
</tr>
<tr>
<td>SGC-68</td>
<td>Si$<em>{0.11}$Ge$</em>{0.88}$C$_{0.01}$</td>
<td>1.5 x 10$^{-3}$</td>
<td>866 ± 5</td>
<td>867</td>
</tr>
<tr>
<td>SGC-69</td>
<td>Si$<em>{0.11}$Ge$</em>{0.88}$C$_{0.01}$</td>
<td>3.0 x 10$^{-3}$</td>
<td>895 ± 9</td>
<td>850</td>
</tr>
<tr>
<td>SGC-70</td>
<td>Si$<em>{0.10}$Ge$</em>{0.88}$C$_{0.01}$</td>
<td>1.5 x 10$^{-3}$</td>
<td>854 ± 7</td>
<td>856</td>
</tr>
</tbody>
</table>

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A model of thin film absorbance in the presence of interference fringes was applied to deduce an absorption coefficient free of interference fringe effects.\textsuperscript{14} The transmittance of a thin absorbing film on a substrate is given by

\begin{equation}
T = \frac{(t_1t_2)^2 e^{-ad}}{1 + (r_1r_2)^2 e^{-2ad} + 2r_1r_2 e^{-ad} \cos(2\phi - \pi)},
\end{equation}

where \(r_1, t_1, r_2, \) and \(t_2\) are the Fresnel reflection and transmission coefficients of the alloy/air and alloy/substrate interfaces, \(\phi = 2nd/(1 + \lambda)\), \(d\) is the alloy layer thickness, and \(\lambda\) is the vacuum wavelength of the incident photons.

For the purposes of data analysis, \(\alpha\) was assumed to be negligible below the energy onset of fundamental absorption. Thus the exponentials of Eq. (1) reduced to unity at sub-gap energies, the amplitude of the fringes was determined solely by the index of refraction \((n)\), and the fringe periodicity \((\phi)\) was determined by \(n\) and \(d\). These parameters were determined by curve fitting the transmittance data in the sub-gap region \((\alpha = 0)\) to the following expression:

\begin{equation}
T = \frac{(t_1t_2)^2}{1 + (r_1r_2)^2 + 2r_1r_2 \cos(2\phi - \pi + \psi)}.
\end{equation}

We have introduced a phase shift fitting parameter \((\psi)\), because we observed a phase shift in the interference fringes and were able to more effectively remove the interference from the absorbance data by including it. In perfect crystals with real indices of refraction, \(\psi\) is expected to be zero. We speculated that the alloy layers were not fully homogeneous, having grain boundaries and voids. Scattering within the alloy layer may be responsible for this phase shift in the interference fringes.

For indirect semiconductors at photon energies below and near the band gap, \(n\) is nearly real and constant.\textsuperscript{15} We fixed \(n\) (hence \(r_1, t_1, r_2, \) and \(t_2\)) in Eq. (1) at the sub-gap values obtained from the fringes, and Newton’s method was applied to solve Eq. (1) for \(\alpha\), given \(T\). This yielded \(\alpha\) free from interference fringes.

Because the smaller values of \(\alpha\) were obscured by noise, curve fitting was adopted to deduce the band gap from the more strongly absorbing energies. The absorption data were initially fit to

\begin{equation}
\alpha = K(E_G - h\nu_m)^m
\end{equation}

with material constant \(K\), band gap \(E_G\), and exponent \(m\) taken as adjustable fitting parameters, to determine the mode of the electron transition. Minimum residual error \((\chi^2)\) yielded \(m=2\) for all samples, indicating indirect band gap materials. For sample SGC-69, which had a significant substitutional C content, the residual error was minimized for 1.9\(<m<2.1\). The fit for the remaining samples converged to \(n=2\) less strongly, with comparable values of \(\chi^2\) obtained for 1.5\(<m<2.0\).

Therefore we fixed the exponent at \(m=2\) and repeated the curve fit to the following relation:

\begin{equation}
\alpha_m = K(h\nu_{pt} + h\nu_{pn} - E_G)^2,
\end{equation}

\begin{equation}
\alpha_e = K \left( \exp \left( \frac{h\nu_{pn}}{kT} \right) (h\nu_{pt} - h\nu_{pn} - E_G)^2 \right).
\end{equation}

FIG. 1. Optical absorption of SGC-69. Experimental data are indicated by a solid line and the best fit of a theoretical indirect absorption curve is indicated by a dashed line. An excellent fit was obtained, and a band gap of 895±9 meV was deduced from this curve fit.

Absorption data and the best fit for sample SGC-69 are illustrated by Fig. 1. The data points were unweighted, so the fitting algorithm favored data points with large values of \(\alpha\). Figure 2 shows a comparison between SGC-69 and SGC-68, a sample with predominantly interstitial C. A sub-gap absorption tail is evident in SGC-68, with the theoretical ab-
crystal was found to impact the energy band gap of the material, which supports the assertion that C may be used to tune the band gap. Substitutional C was found to increase the band gap at this composition. Other workers have found C decreases the band gap with respect to a Si$_{1-x}$Ge$_x$ alloy. However, other work has been limited to Si rich alloys, and the band gap may in fact decrease with increasing substitutional C at those compositions. Thus, this work is not necessarily inconsistent with previous results.

The location of C within a Ge rich Si$_{1-x-y}$Ge$_x$C$_y$ lattice is evidently dependent on the growth conditions. The ability to manipulate the growth conditions to increase the substitutional C incorporation will allow the Si$_{1-x-y}$Ge$_x$C$_y$ band gap and lattice constant to be engineered over a wider compositional range.

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